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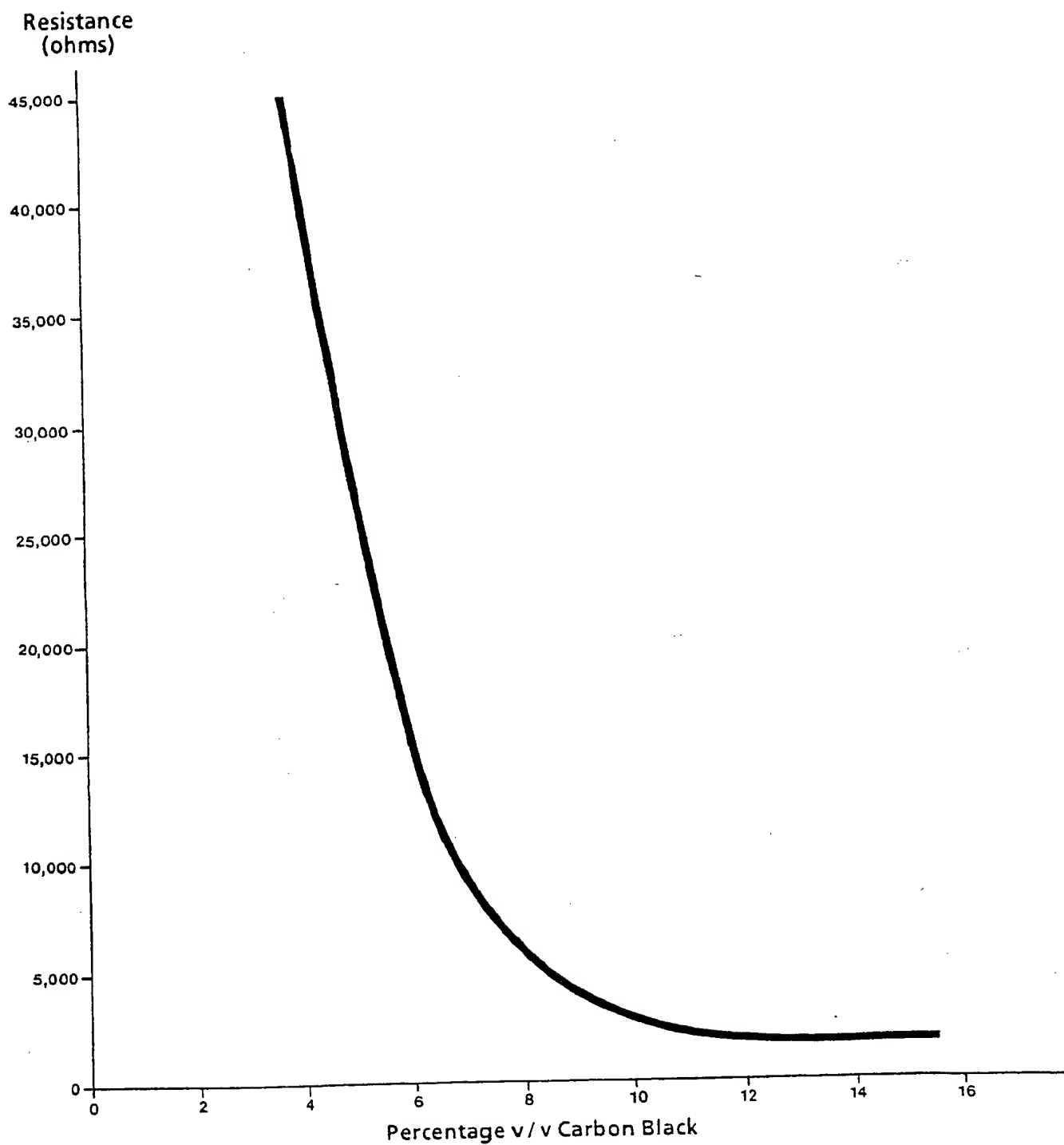
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(54) Coating composition

(57) An electrically conductive water-based coating composition comprises carbon black or other electrically conductive filler incorporated into an aqueous polyurethane elastomer dispersion in such proportions that application of the composition to a support surface can form an abrasion resistant and electrically conductive coating thereon. This minimises the risks of explosion arising as a result of accumulation of static electrical charge particularly during the handling of powdered materials or flammable solvents. The provision of an abrasion resistant coating gives further advantage of longer working life before re-coating is required.

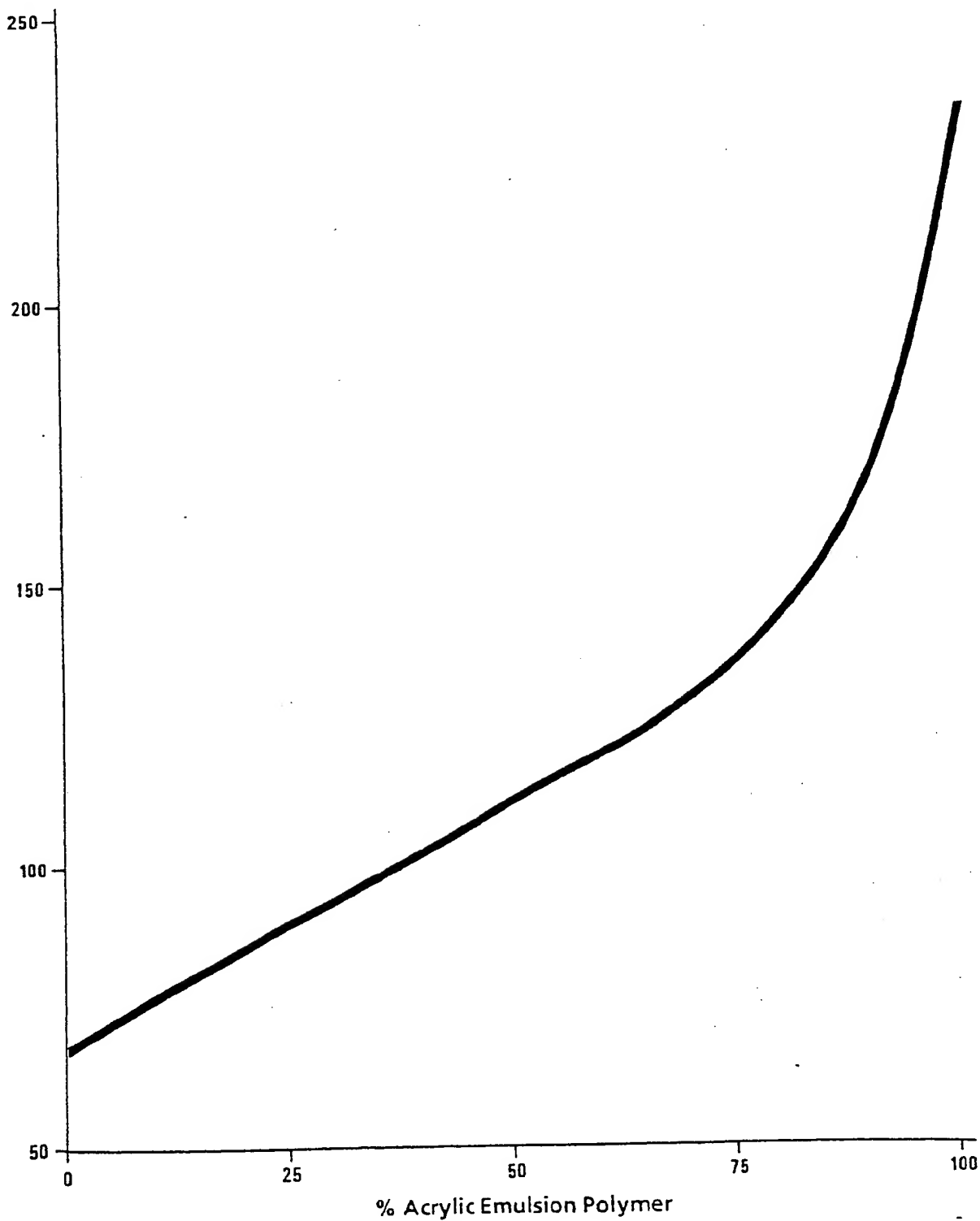
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GRAPH 1 RESISTANCE OF ELECTRICALLY CONDUCTING COATINGS CONTAINING VARIOUS PERCENTAGES BY VOLUME OF CARBON BLACK IN THE DRIED FILM.



GRAPH 2 ABRASION RESISTANCE OF ELECTRICALLY CONDUCTING COATINGS BASED ON BLENDS OF POLYURETHANE ELASTOMER DISPERSION AND ACRYLIC EMULSION POLYMER.

Abrasion Resistance
Mg loss / 1000 cycles



COATING COMPOSITION

This invention relates to a coating composition which can be applied to a support surface in order to form an abrasion resistant and electrically conductive coating thereon.

It is well-known in the art that non-conducting organic polymer coatings can be made electrically conductive by the incorporation of conductive filler particles such as silver, copper, nickel, carbon black, etc. Historically, such coating compositions have been solvent based, but, because of this solvent content, have a number of disadvantages. Because of the relatively low flash point of most common organic solvents, virtually all solvent based coatings will present some form of flammability hazard. In certain instances, where solvents with particularly low flash points are utilised, such compositions may even have to be classified as highly flammable. Solvent based products also give rise to adverse health effects due to inhalation of solvent vapours during application and the subsequent drying of the coating film. In such instances the liquid applied coating is converted to the solid state by the evaporation of relatively large volumes of solvent, which, unless adequate natural or mechanical ventilation is provided, can quickly result in such effects as dizziness and nausea or, on prolonged exposure, more serious health defects. Where adequate natural or mechanical ventilation cannot be provided, therefore, it is generally necessary for personnel applying such coatings to wear appropriate personal protective equipment in the form of cartridge type ventilator masks or air fed hoods to eliminate the risk of inhalation of the harmful solvent vapours. Even where such precautions are taken, however, the period over which the solvent vapours continue to be evolved from the coating are generally considerable, which often leads to delays before

the area being treated can be reoccupied for normal working practices. Similarly, where such coating compositions are used in food processing plants, the evolution of solvent vapours can give rise to serious problems of tainting of the food-stuffs. Furthermore, as environmental awareness and legislation around the world has increased it is widely accepted that there is a need to control the evolution of volatile organic compounds into the atmosphere.

In view of the above factors, in recent times electrically conductive coatings have been formulated based upon water based emulsion polymers. Because of the nature of the colloidal polymer dispersions involved, however, such coating compositions offer only poor to moderate abrasion resistance and are, as a result, totally unsuited for use in aggressive environments where severe abrasion conditions would be expected.

One of the major advantages of electrically conductive coatings is their ability to eliminate problems of explosion which can be caused by dangerous accumulations of static electric charge. One example of this is the emptying of powder from paper or plastic sacks where it has been demonstrated that a dangerous accumulation of electric charge can occur unless suitable precautions are taken. As the sack is emptied, sufficient charge can accumulate to produce a large potential difference between the sack and earth which can result in an electrostatic discharge between the sack and a nearby earthed object. This, in turn, can result in fire or explosion, particularly where flammable materials may be in the vicinity.

Explosives stores are a further example of areas where static build-up can be a serious hazard. For example, the magazine areas within naval fighting vessels are generally constructed of steel plate. In the event that a metallic object is dropped onto the steel surface, sparks can result and so it is desirable to coat the steel with a non-metallic coating. Conventional coatings, however, because

of their insulating properties can result in static build-up with the potential for spark discharge. Clearly, in such a situation this will be highly undesirable and the use of a conductive coating to protect the metal surfaces is essential. Application for such a material, however, can be seen in any situation where explosive materials are stored and there is a risk of static build-up.

A further example of the use of conductive coatings would be in areas where flammable solvents were being either processed or stored. For example, the steps and walkways on solvent storage tanks could be treated in order to eliminate static discharge from personnel who may have to carry out maintenance on the tanks or who are involved when the tanks are being filled.

In each of the situations described above it can be seen that in addition to the coating being electrically conductive it must also be durable and abrasion resistant to maintain its effectiveness. For example, in an industrial environment where solid handling is being carried out, severe abrasion can result from pedestrian and vehicular traffic in combination with the abrasive influences of the solids themselves. In magazine areas, for example, the situation can exist where heavy equipment might be dragged over the coated surface leading to scratching and penetration of the coating. This could quite clearly lead to sparks in its own respect and over time could result in the coating being worn away.

Similarly, where coatings are applied to metal steps or walkways on tanks it is clear that these coatings will need to be highly abrasion resistant if they are to remain in place for any considerable period of time. In this respect, conventional water based paints such as those based upon commonly used emulsion polymers, e.g. acrylics, styrene acrylics, styrene butadiene copolymers, vinyl acetate-ethylene-vinyl chloride terpolymers, etc. or even conventional cross-linked coatings such as water

dispersible epoxy systems, fail to provide the durability and abrasion resistance required.

It is a further advantage of electrically conductive coatings that they are known to reduce the risk of disruption to sensitive electronic components by electromagnetic wave interference (EMI) or radio frequency interference (RFI). The use of a durable electrically conductive coating is desirable in areas such as the floors of computer rooms where there will be considerable pedestrian traffic, or, on work benches where sensitive electronic equipment might be being assembled, and in which there would otherwise be risk of damage to the coating by scratching or manual abrasion if the coating did not possess adequate abrasion resistance.

It is an object of the invention to provide a coating composition which is capable of forming an electrically conductive coating on a support surface and which has improved abrasion resistance.

According to the invention there is provided an electrically conductive coating composition which comprises carbon black filler incorporated into an aqueous polyurethane elastomer dispersion in such proportions that application of the composition to a support surface can form an abrasion resistant and electrically conductive coating thereon.

Preferably, the dispersion is a colloidal dispersion.

The abrasion resistance properties of the applied coating may be improved by including a suitable cross-linking agent. A preferred cross-linking agent is a polyaziridine or a polycarbodiimide.

The nature of the aqueous polyurethane elastomer dispersion may vary considerably, being either based upon aromatic, aliphatic or cycloaliphatic isocyanates, and containing various polymer backbones such as polyether, polyester, or polycarbonate. In each instance, however, good abrasion resistance is obtained without the

disadvantage of conventional two component polyurethane systems or moisture cured polyurethane systems where free isocyanate groups are present.

To further improve abrasion resistance it is a preferred aspect of this invention that the polyurethane elastomer dispersions should contain functional groups such as carboxylic acid to allow modification with various cross-linking agents. Examples of such materials which can be used are polyaziridines such as trimethylolpropane-tris-(beta)-(N-aziridiny) proprionate and pentaerythritol-tris-(beta)-(N-aziridiny) proprionate or polycarbodiimides such as Ucarlink XL-25 SE ex Union Carbide.

The use of such materials results in the carbon black containing polyurethane elastomer dispersion being converted into a more highly cross-linked polymer matrix which significantly improves toughness, durability and abrasion resistance. Whilst the carbon black containing polyurethane elastomer film itself, therefore, possesses significantly improved durability and abrasion resistance over conventional water based coating compositions, when cross-linked in the manner indicated, the properties in this respect are dramatically superior, thus making these products ideally suited for use as electrically conducting coatings in environments subject to abrasion.

For certain applications slightly lower abrasion resistant properties might be acceptable, and in these instances the polyurethane elastomer dispersions may be modified by a proportion of a conventional lower cost emulsion polymer such as an acrylic. Advantageous abrasion resistant properties can still be obtained when the proportion of modifying emulsion polymer is as high as 75% by weight.

It is a further advantage of such compositions that their abrasion resistant properties are developed extremely quickly and, as a result, applications can be put back into service within 24 hours under normal circumstances. This,

coupled with the water based nature of the product means that applications can be carried out without need to preclude access of personnel to adjacent areas.

Whilst most carbon blacks are likely to give some degree of conductivity, it is known that certain forms of carbon black give rise to greater electrical conductivity than others. The most effective carbon blacks from the standpoint of providing electrical conductivity are those with a high surface area and high pore volume. The pore volume is typically measured by the absorption of dibutylphthalate and gives information on the void volume between the carbon black particles that form aggregates. These are clusters of carbon black particles that are strongly attached to one another by physical forces (e.g. van der Waals forces). The aggregates, in turn, are clustered to so called agglomerates which are held together by weaker forces. It is this agglomeration of carbon black particles which results in good electrical conductivity. Furthermore, certain specialist carbon blacks are particularly highly conductive due to the fact that they consist of hollow shell-like particles instead of solid particles. This results in an even larger surface area and pore volume, and, consequently an even higher electrical conductivity per unit weight of carbon black.

The electrical conductivity of a carbon black containing coating, however, does not just depend upon the quantity and type of carbon black present, it is also very much dependent upon the nature in which the carbon black is processed. Insufficient processing can result in uneven dispersion and a consequential variation in electrical conductivity across the applied coating. Over processing, i.e. the application of excessive shear forces during compounding, can result in breakdown of the carbon black agglomerate structure. In this respect, it is advantageous to compound the carbon black into the electrically conducting coating composition by way of a water based

predispersion. An example of such a material is Ketjenblack EC-310 NW. and in this form the material can then be simply stirred into the polyurethane elastomer dispersion under low shear to ensure optimum particle distribution without breaking down the carbon black agglomerates.

The degree of electrical conductivity is dependent, therefore, on the nature of the carbon black, the degree of dispersion and also the level of incorporation. With regard to the latter, it is generally observed that providing that the carbon black is dispersed optimally, the electrical conductivity will increase with addition level up to a certain level, and then will plateau. The preferred level of carbon black in the dry film of the polyurethane elastomer is between 9.0% and 15.0% by volume. A particularly preferred level is 12.5% by volume.

To improve the application characteristics of the electrically conducting coating composition, the rheology of the material is controlled by the use of a suitable thixotroping agent. One example of a particularly effective thixotroping agent is Rheolate 255 ex Kronos Titan GmbH. In the case of this material, the preferred level of addition is 2.0% by weight.

In view of the fact that the coating compositions of the invention will frequently be applied to steel surfaces, it is a preferred embodiment of the invention that it should incorporate a flash rust inhibitor to avoid problems of rust bleed through the coating. One example of such a material which can be used for this purpose is 3-amino-2-methylpropanol, the preferred addition level of this material being 1.0% by weight.

As a means of imparting opacity to the coating whilst at the same time modifying the colour, an additional preferred embodiment of the invention is the incorporation of titanium dioxide at a level of between 1.0% and 10.0% by weight.

A further preferred embodiment of the invention is the incorporation of a suitable silicone additive to ensure good surface wetting, freedom from cissing and to promote scratch resistance. One example of a particularly effective material in this respect is ByK 306, ex Byk Chemie, with the preferred addition level being in the range of 1.0 to 2.5% by weight.

Examples of electrically conductive water based coating compositions according to the invention will now be described in detail. It should be understood that the specific materials disclosed and their proportions are for illustrative purposes only.

Example 1

The effect of carbon black addition level on the electrical conductivity of the experimental coatings was determined as follows. A clear unpigmented coating composition was prepared by blending together 100 p.b.w. of a 35% w/w aliphatic polyurethane elastomer dispersion with 2.8 p.b.w. of a trifunctional aziridine cross-linking agent having a molecular weight of 467.

Quantities of this blend were immediately mixed thoroughly with a 10% dispersion of highly conductive carbon black (Ketjenblack EC-310 NW, ex AKZO Chemie) in varying proportions. The coating compositions thus produced were then brush applied onto a non-conductive quarry tile surface to give a dry film thickness in each instance of approximately 25 microns. Once the applied coatings had dried thoroughly, the electrical resistance across the surface of the coating was measured by taking readings with a Multimeter, the contacts being positioned at a distance of approximately 2 inches apart in each instance. Ten such readings were taken with an average of the results obtained being calculated, together with the range of deviation. The findings were as follows:

<u>Coating</u> <u>Composition</u>	<u>Percentage Carbon</u>		<u>Resistance</u>	<u>Deviation</u>
	<u>Black in Dried Film</u>			
	(w/w)	(v/v)	(ohms)	(\pm ohms)
A	6.69	3.62	45.000	5.000
B	8.72	4.77	27.000	2.000
C	10.94	6.06	13.000	1.000
D	13.37	7.49	8.000	500
E	16.05	9.11	3.000	100
F	22.28	13.08	1.600	50
G	25.94	15.53	1.600	50

Coating compositions and test panels outside this carbon black range were prepared, but at higher levels film formation was adversely affected whilst at lower levels a conductivity reading could not be obtained with the test equipment being utilised.

The results obtained, are presented in Graph 1 which shows the preferred range for the carbon black addition level to be between 9.0% and 15.0% by volume of the dried film, with a particularly preferred level being 12.5% by volume.

Example 2

The importance of the nature of the water based polymer utilised from the standpoint of the abrasion resistance of the coating compositions can be seen by comparing the resistance to sliding abrasion of systems based on typical polymers. Thus, coating compositions were produced in which Ketjenblack EC-310NW was added to the polymer system in such proportions to give a carbon black loading of 22.58% by weight of the dry film in each instance. The following polymer systems were employed:

<u>Composition</u>	<u>Polymer System</u>
H	Aliphatic polyurethane elastomer dispersion cross-linked with trifunctional aziridine.
I	Water dispersable epoxy-polyamide system.
J	Carboxyl functional acrylic emulsion polymer cross-linked with water dispersable epoxy resin.
K	Styrene-acrylic emulsion polymer.

Evaluation of the abrasion resistance of the above compositions was carried out using a Teledyne Taber abraser. Four-inch square mild steel panels with a one eighth inch diameter hole drilled centrally were abraded with coarse emery paper and cleaned and degreased with 1,1,1-trichloroethane before the experimental coating compositions were applied by brush. Multiple coats were applied to give a sufficiently thick coating to enable Taber abrasive wear testing to be carried out over several hundred cycles. Taber abrasion measurements were carried out under dry conditions using CS17 calibre wheels and a 1kg load.

After wearing a track into the surface of the coated panels, the wheels were refaced before running for a number of sets of 100 cycles, refacing the wheels after each run. Weight measurements were taken before and after each run in order that the total weight loss could be calculated. The results for the four coating compositions described above are as follows:

	H	I	J	K
Weight loss per 1000 cycles (mg)	66	308	270	380

Example 3

The importance of the presence of cross-linking agent was demonstrated by comparing the abrasion resistance of composition "H" with a similar composition excluding the

cross-linking agent (composition "L"). Taber abrasion test panels were prepared as described in Example 2 using the above coating compositions, which, on Taber abrasion testing using CS17 wheels and 1kg load under dry conditions, gave the following results:

	H	L
Weight loss per 1000 cycles (mg)	66	103

Thus it can be seen that significantly improved abrasion resistance is obtained when the cross-linking agent is present.

Example 4

The effect of modification of the polyurethane elastomer dispersion with a conventional lower cost emulsion polymer was demonstrated by substituting 20% by weight (composition "M"), 67% by weight (composition "N") and 100% by weight (composition "O") of the polyurethane elastomer dispersion in composition "H" by a carboxyl functional acrylic emulsion. Taber abrasion test panels were prepared as described in Example 2 using each of the coating compositions which, on Taber abrasion testing using CS17 wheels and 1kg load under dry conditions gave the following results:

	H	M	N	O
Weight loss per 1000 cycles (mg)	66	91	124	233

The results obtained are presented in Graph 2 which shows that advantageous abrasion resistant properties can still be obtained even when the proportion of the lower cost modifying polymer is as high as 75% by weight.

Example 5

To improve application characteristics by reducing the risk of dripping and sagging of the wet applied coating, Composition "H" was modified by the addition of Rheolate 255, a polyurethane thickening agent. Addition levels of 1% by weight (Composition "P"), 2% by weight (Composition

"Q") and 3% by weight (Composition "R") were considered. Composition "P" failed to develop adequate structure, whilst Composition "R" resulted in brush marking of the applied film. Composition "Q" gave good application characteristics and flow and an addition level of 2% by weight is, therefore, preferred.

Example 6

Composition "Q" was further modified by the addition of 3-amino-2-methylpropanol to reduce the risk of flash rusting when applying the coating composition to steel substrates. Addition levels of 0.5% by weight (Composition "S"), 1.0% by weight (Composition "T") and 1.5% by weight (Composition "U") were considered, the compositions being applied to mild steel panels which had been manually abraded to a bright metal finish with coarse emery paper. Flash rusting was observed at 0.5% addition level but was not evident with Compositions "T" and "U". The preferred addition level is, therefore, 1.0% by weight.

When, as is preferred, the coating composition includes a cross-linking agent, i.e. the polyurethane elastomer conductive coating composition is cross-linked with a reactive moiety, it will be necessary to supply the composition as a two component mix.

In this specification, reference is made to the use of carbon black filler to be incorporated in an aqueous based polyurethane elastomer dispersion so as to form a conductive coating, and it should be understood that carbon black is a presently preferred conductive filler material.

It is envisaged, however, that other electrically conductive filler materials may be incorporated to advantage in the dispersion to enable the formation of an acceptable abrasion resistant and electrically conductive coating.

CLAIMS

1. An electrically conductive water based coating composition which comprises carbon black filler incorporated into an aqueous polyurethane elastomer dispersion in such proportions that application of the composition to a support surface can form an abrasion resistant and electrically conductive coating thereon.
2. A composition according to Claim 1, in which the dispersion is a colloidal dispersion.
3. A composition according to Claim 1 or 2, in which the composition includes a cross-linking agent.
4. A composition according to Claim 3, in which the dispersion includes functional groups capable of reacting with the cross-linking agent.
5. A composition according to Claim 3 or 4, in which the cross-linking agent comprises a polyaziridine or a polycarbodiimide.
6. A composition according to any one of Claims 1 to 5, in which the aqueous polyurethane elastomer dispersion is based upon aromatic, aliphatic or cycloaliphatic isocyanates.
7. A composition according to Claim 6, in which the dispersion includes a polymer backbone.
8. A composition according to Claim 7, in which the polymer backbone comprises polyether, polyester or polycarbonate.
9. A composition according to any one of Claims 1 to 8, in which the dispersion is modified by a proportion of an emulsion polymer.
10. A composition according to Claim 9, in which the emulsion polymer is an acrylic.
11. A composition according to Claim 10, in which the modifying acrylic emulsion polymer has carboxyl functionality.
12. A composition according to any one of Claims 9 to

11. in which the proportion of emulsion polymer in the dispersion is up to 75% by weight.

13. A composition according to any one of Claims 1 to 12, in which the proportions of carbon black in the composition are such that the level of carbon black in the dried coating is between 9% and 15% by volume.

14. A composition according to Claim 13, in which the proportions are such that the level of carbon black in the dried coating is 12.5% by volume.

15. A composition according to Claims 1 to 14, in which the composition includes a rust inhibitor to render the composition suitable for coating a steel, iron or other ferrous surface.

16. An electrically conductive water based coating composition which comprises electrically conductive filler material incorporated into an aqueous polyurethane elastomer dispersion in such proportions that application of the composition to a support surface can form an abrasion resistant and electrically conductive coating thereon.

17. A composition according to Claim 1 and substantially as described herein and with reference to any one of the Examples.